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1

PHOTOTHERMAL SPECTROSCOPY USING A PYROELECTRIC THIN FILM DETECTOR

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ABSTRACT: The application of pyroelectric thin film transducers for photothermal studies is described. The sensitivity and versatility of pyroelectric detection is demonstrated by spectroscopic studies of neodymium oxide doped poly(methyl methacrylate) films. At energy fluences of less than 10 mJ/cm^2, sensitivities of 10^{14} molecules/cm^2 are achieved with a conventional amplitude modulated light source as well as with a pulsed laser. A detector response time of less than 100 ns is observed with pulsed excitation.
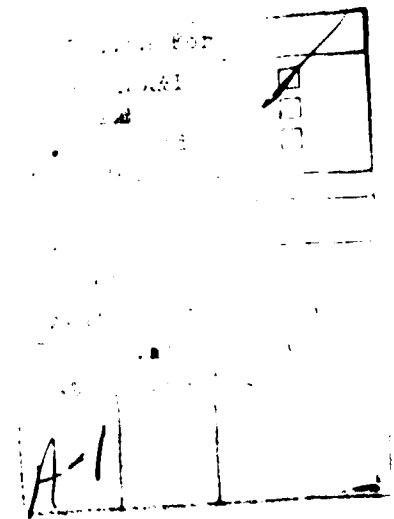
Photothermal [1] and photoacoustic techniques [2] rely on the detection of thermal or acoustic waves generated by the absorption of electromagnetic radiation and subsequent radiationless deexcitation. Several detection schemes have been developed in the past that allow highly time resolved and sensitive detection of these effects. The temperature rise at the surface of a solid sample can be determined, for example, directly by a sensitive infrared detector via an increase of black-body radiation [3]. In a gas or liquid that is in contact with the sample, a temperature gradient develops. This causes a refractive index gradient which can be probed by a second light source [4]. Due to thermal expansion, acoustic waves are generated in the sample, at its surface or the surrounding medium forming the basis of various photoacoustic detection methods. They used to be dominated by microphones, but piezoelectric transducers replaced them in most applications. With piezoelectric transducers, time resolutions in the order of 10 ns [5] and sensitivities of a fraction of a monolayer [6] have been achieved. Photothermal techniques promise similar results [7] and have the advantage of measuring the energy deposited in the sample directly without requiring mechanical contact of sample and detector. More conventional techniques like calorimetry [8] or bolometers [9] have rarely been used for the detection of thermal wave phenomena. Only recently, calorimeters have been employed to demonstrate the feasibility of photothermal microscopy [10] and spectroscopy of adsorbates [11] with pyroelectric detectors. In these exploratory studies, $LiTaO_3$ single crystals or PZT® ceramics with a heat capacity in the order of 0.6 J/K resp. 0.07 J/K were used as thermometers. These studies showed that a suitable pyroelectric calorimeter could combine some of the advantages of photothermal detection schemes - direct measurement of the radiation induced temperature increase - with most features of the well established piezoelectric transducers, that can be readily attached to a sample and have high sensitivities or time resolution, thus complementing the existing detection schemes.

For a calorimeter to be useful as a sensitive thermometer, the heat capacity has to be low, *i.e.*, it should have a small mass and be made out of a material with low specific heat. If the temperature change will be detected as an electric signal via the pyroelectric effect, the pyroelectric coefficient of the detector material should be large, its dielectric constant small. A combination of these properties can be represented by a pyroelectric figure-of-merit [12]. Besides the material properties, the geometry of the calorimeter is essential. Its coupling area to the sample should be large to facilitate thermal contact and it should be thin to achieve a fast thermal response; thermal leakage should be minimized by the design of the detector. As far as the material properties are concerned, $Li_2SO_4H_2O$ would be the material with the highest figure-of-merit [12]. Being a brittle single crystal, it is, however, hard to handle and extremely difficult to machine. A readily available ferroelectric polymer like polyvinylidene difluoride (PVF_2) has a slightly lower figure-of-merit - 9.7 [3] - as compared to 15.2 for $Li_2SO_4H_2O$ [12] or 0.02 for PZT® [2]. It is, however, at cost of $0.20/cm^2$ readily available in thicknesses down to 6 μm, it is easy to handle and can be attached to flat as well as curved surfaces. This makes it a prime candidate for a pyroelectric thermometer that can be attached to all types of samples or can serve as a substrate for studies or thin films and adsorbates.

In this study, 9 μm thick ferroelectric PVF_2 foils with nickel electrodes (Pennwalt Kynar[TM]) were used. The PVF_2 film is supported around its perimeter (8 mm diameter) by metal washers. They serve as mechanical support, as heat sink and as electrical contacts. The heat capacity of the PVF_2 film, as determined with a conventional differential scanning calorimeter at 22°C, was in the order of 2 mJ/K, the detectivity typically 100 mV/K. PVF_2 itself is transparent in the spectral range considered in this study. Due to the two

nickel electrodes, however, the detector transmits at a wavelength of 632.8 nm only 8.4 % of the incident light, 38.0 % are reflected.

For the evaluation of detectors rare earth oxide samples are particularly suitable[2] because of a large number of sharp transitions. Samples were prepared from 99.99 pure, 400 mesh neodymium oxide powder (Atomergic Chemetals Corporation). One drop of a dispersion of 1 mg Nd_2O_3 in 1g poly(methyl methacrylate) (PMMA) dissolved in 10 ml of chlorobenzene was spin coated onto the detector or a substrate. The film thickness is determined by weighing to be 8.5 ± 0.1 μm with excellent reproducibility. Assuming constant Nd_2O_3/PMMA ratio, this corresponds to 0.8×10^{15} Nd_2O_3 molecules in a 8 mm diameter sample area. This number of Nd_2O_3 molecules is equivalent to 1 monolayer.

Low Frequency Amplitude Modulation

Broad band spectra in the visible spectral region were recorded using a conventional photoacoustic spectrometer. A current modulated xenon high pressure lamp (CERMAX VIX 300 UV) and a 1/4m, f/4 scanning monochromator were used as excitation source. Spectra were recorded with 5 s^{-1} square wave modulation and 3 nm bandwidth at a scanning speed of 100 nm/min. Three detectors are excited simultaneously using beam splitters: an uncoated element with 45% of the light flux, the sample under study with another 45% and a third one, coated with a 100 μg/cm^2 carbon glass film as reference [14] with the remaining 10%. The difference between sample and uncoated detector is amplified with a differential input lock-in amplifier (EG&G 5206). It is normalized with the signal from the carbon coated reference detector which has been demodulated by a second lock-in amplifier.

Figure 1 shows the normalized difference spectrum of Nd_2O_3 in PMMA. Spectral features reported previously for much higher concentrations of Nd_2O_3 powder in a

cyanoacrylate matrix [15] are clearly visible. Superimposed are fringes due to different thicknesses of coated and uncoated sample. To demonstrate the versatility and flexibility of this thermal wave detector, the front side of a 1 mm thick, undoped PMMA calotte, 100 mm radius of curvature, was coated with Nd_2O_3 doped PMMA, the detector attached to the backside of the sample. The resulting normalized difference spectrum (Fig. 2) shows the same spectral features as the previous one, but inverted. Light absorbed by Nd^{3+} contributes less heat than light absorbed in the nickel electrodes due to thermal damping in the 1 mm thick PMMA substrate. This exemplifies the depth profiling capability of photothermal spectroscopy [2] but also the problems in the interpretation of these spectra.

Pulsed Excitation

Pulsed excitation offers two main advantages [16]: the availability of continuously tunable lasers in the the complete spectral range from UV into the IR and the direct access to time domain information, like lifetimes or relaxation times. To demonstrate the potential of the pyroelectric thin film detector, it was excited with an excimer laser pumped dye laser system (Lamdaphysik EMG201, FL2002) with a pulse width of 12 ns. The Gaussian beam, expanded to a diameter of 10 mm, impinges on the detector at an angle of 75°C from the surface normal; the pulse energy incident on the detector is typically 10 mJ. A custom designed preamplifier (Comlinear CLC-B-600) with a rise time of 450 ps, a Tektronix 7912 transient digitizer and a Dataprecision D6000 wave form analyzer were used to record and analyse the time dependent signals.

With approximately 5 mJ of the laser energy absorbed, mainly in the electrodes, one would expect a temperature rise of 2.5K in the calorimeter resulting in a 250 mV signal amplitude. This is in excellent agreement with the observed amplitudes of 100 mV with a 50Ω input impedance (Figs. 3 and 4). The rise time of the signal is less than 100 ns

(Fig. 3), the decay time 10 to 100 ms (Fig. 4) depending on the gas in contact with the detector. The observed pulse shape is consistent with calculations of laser heating of solid targets [17]. These data underline the important features of this calorimeter: fast response allowing time resolved studies and low thermal leakage making it ideal for thermometric applications. The signal is unipolar, quite different from the typical ringing of the piezoelectric transducers [2]. Real time compensation of the signals of two transducers, being crucial for studies of adsorbed species [11], is straightforward for a unipolar signal like the one shown in Fig. 4, but almost impossible for two ringing signals. With a ringing signal, normally a gated integrator is used to integrate over part of the largest peak. If the signal is, however, unipolar, the integration can be extended over the complete signal, resulting in a superior signal/noise ratio.

The result of an experiment on Nd_2O_3 in PMMA at 300K is shown in Fig. 5. The dye laser is scanned in steps of 0.05 nm at a spectral resolution of 0.006 nm through its tuning range. A coated and an uncoated sample are illuminated simultaneously, the difference signal is digitized and integrated. For comparison absorption data of Nd^{3+} in Y_2O_3 taken at 4.2K are shown [18], they are corrected for the wavelength dependence of the laser power.

The difference in temperature, which causes linebroadening and in addition, due to a change in ground state population, a change of the relative intensities as well as the different host crystals account for the observed differences. The noise in the photothermal spectrum is a clear evidence of the sensitivity of this type of detector far beyond the monolayer coverage shown.

Conclusion

A comparison of the pyroelectric with the piezoelectric detection scheme shows that both techniques have similar sensitivities and response times. The thermal wave detector can, however, easily be calibrated with a conventional calorimeter. It is not subject to acoustic noise or mechanical resonances. It has a flat response in the range 10^{-1} K/s to 10^7 K/s accessible in this study. It has a unipolar signal that can be readily compensated by the signal from a second detector or be integrated to improve the signal/noise ratio.

Acoustical waves are essentially unattenuated in the frequency range studied with photoacoustic techniques. Acoustic delay lines can therefore be implemented to separate electromagnetic interference due to the laser discharge from the signal without affecting the signal amplitude. But evidently, the acoustic impedances of sample, delay line, and detectors have to be matched to avoid reflections, a problem that is not encountered with thermal waves. In conclusion, pyroelectric detection of thermal waves using a thin film detector is a fast and sensitive alternative for the measurement of transient surface temperature phenomena complementing other photothermal and photoacoustic techniques.

Acknowledgment

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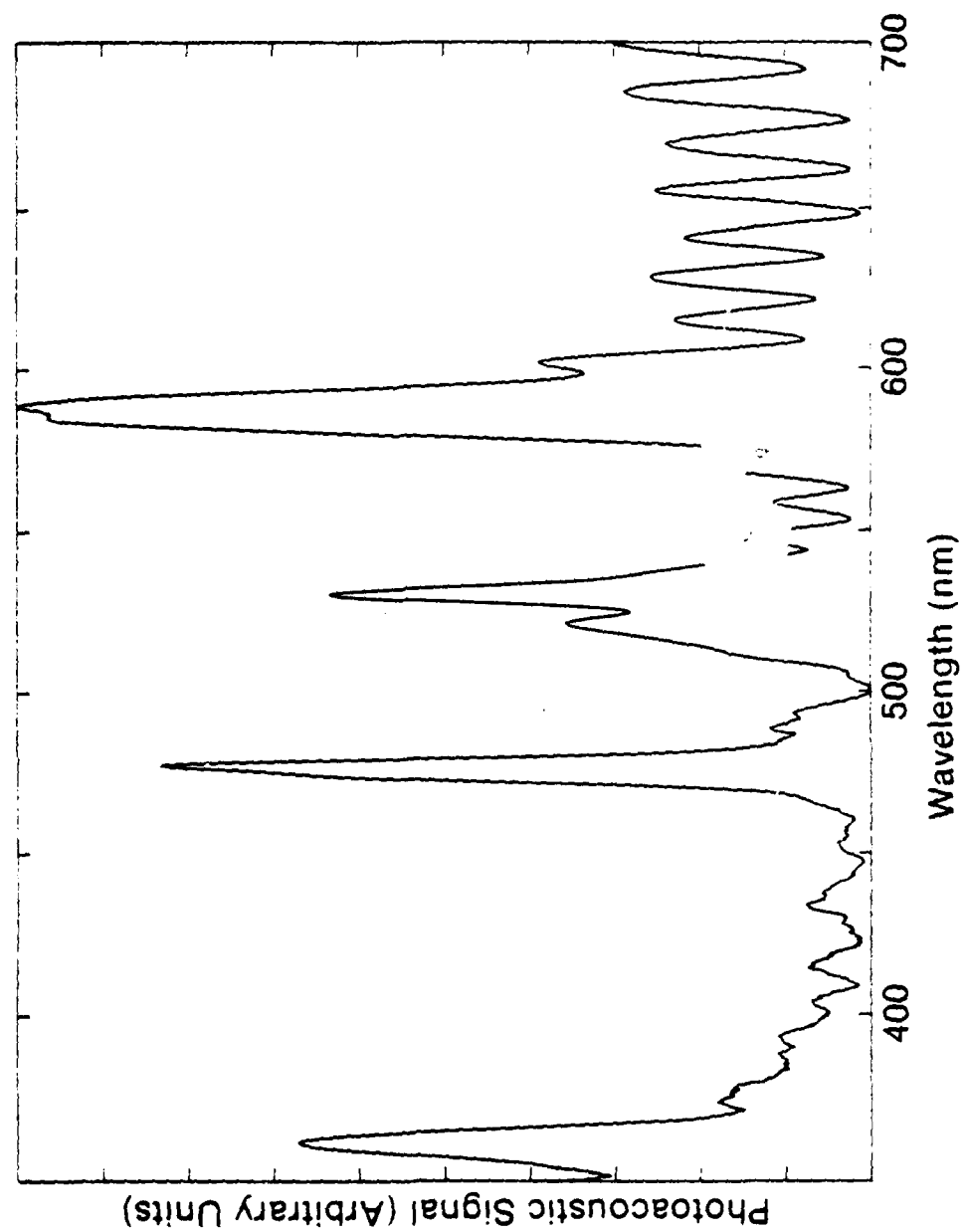18. N. C. Chang, *J. Chem. Phys.* 44, 4044 (1966).

Figure 1. Photothermal absorption spectrum of 0.8×10^{15} Nd_2O_3 molecules isolated in a 10 μm thick PMMA matrix recorded with a conventional scanning spectrometer, resolution 3 nm.
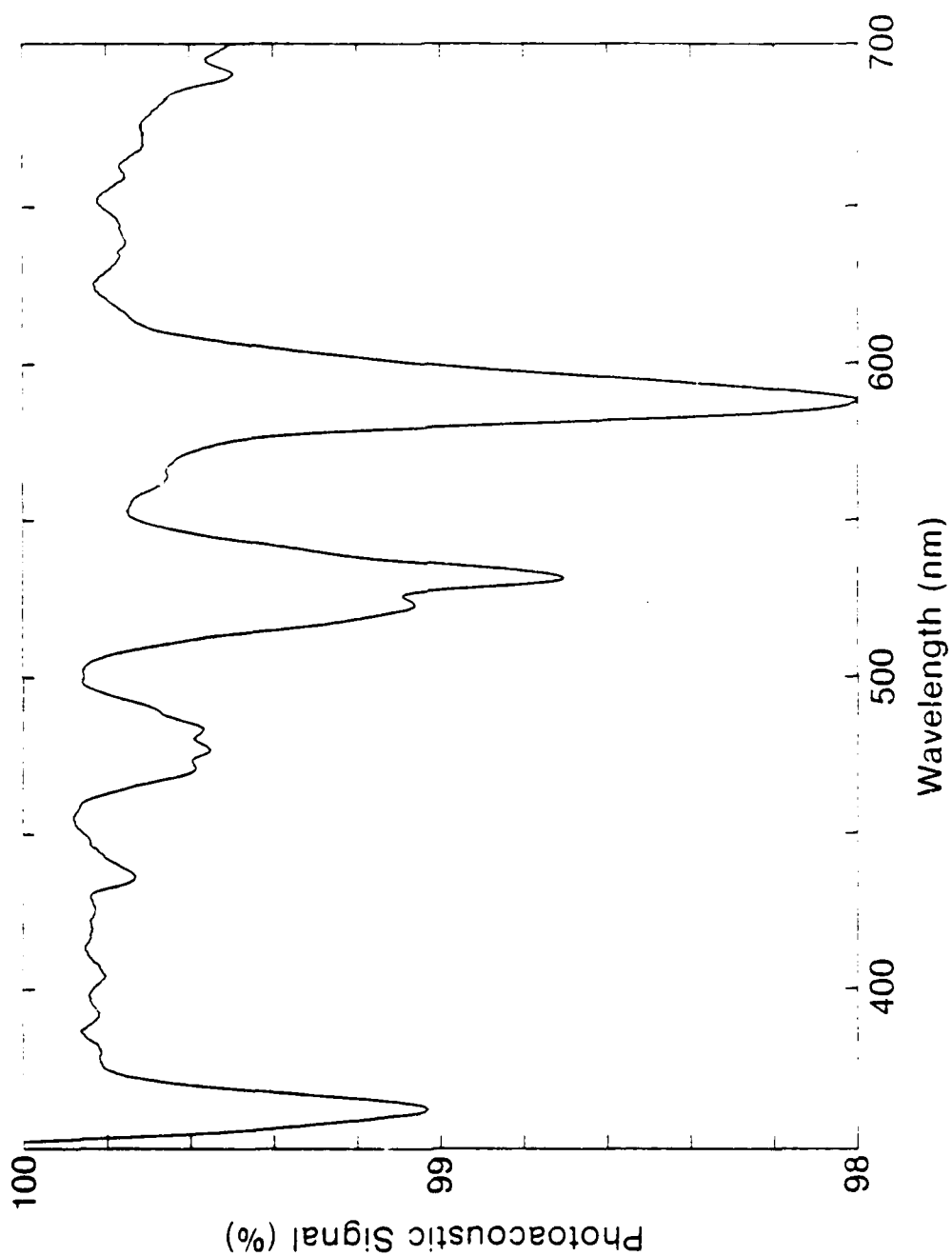
Figure 2. Photothermal transmission spectrum of 0.8×10^{15} Nd_2O_3 molecules isolated in a 10 μm thick PMMA matrix on a 1 mm thick curved PMMA substrate recorded with a conventional scanning spectrometer.
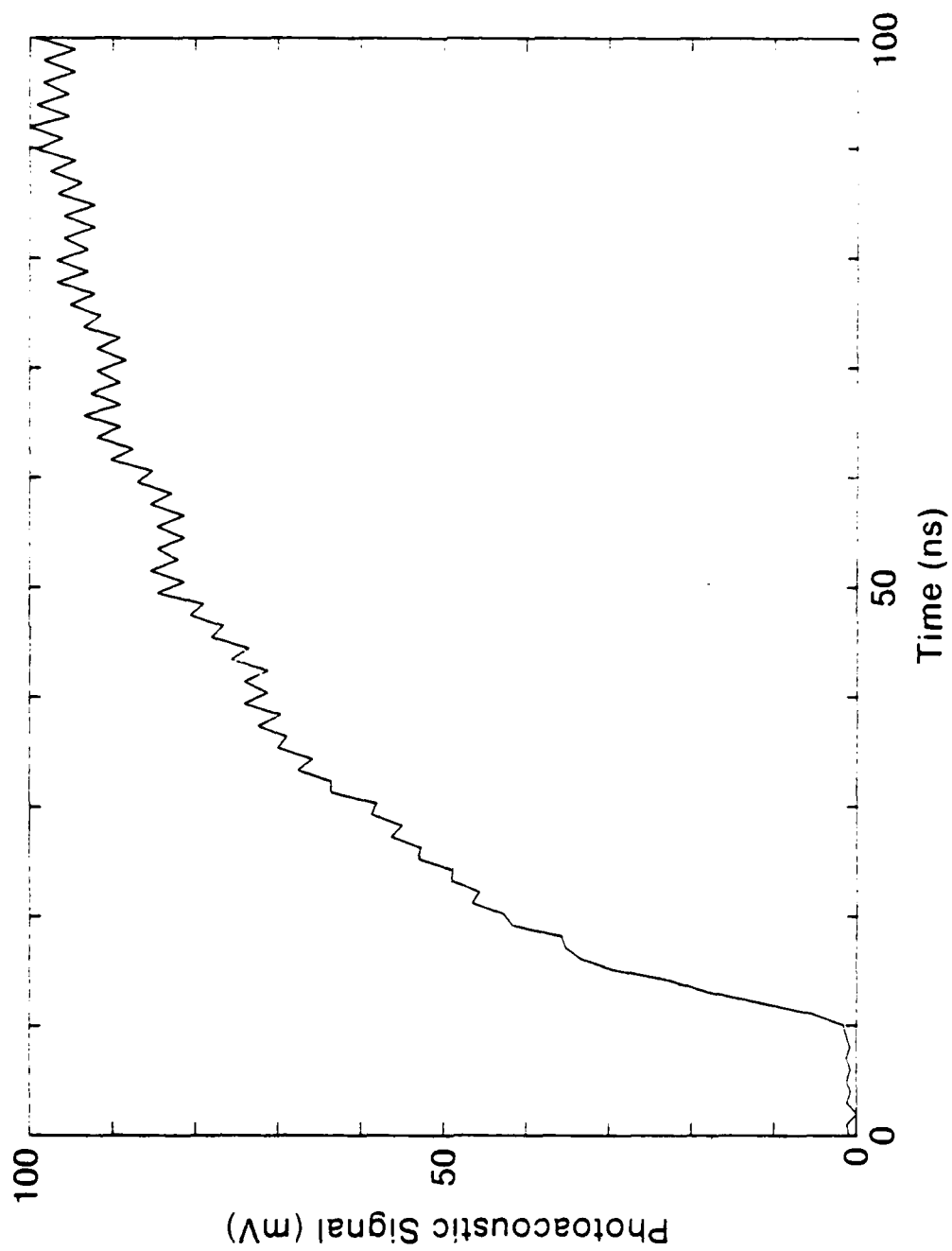
Figure 3. Response of the calorimeter to a 10 mJ, 12 nsec laser pulse.
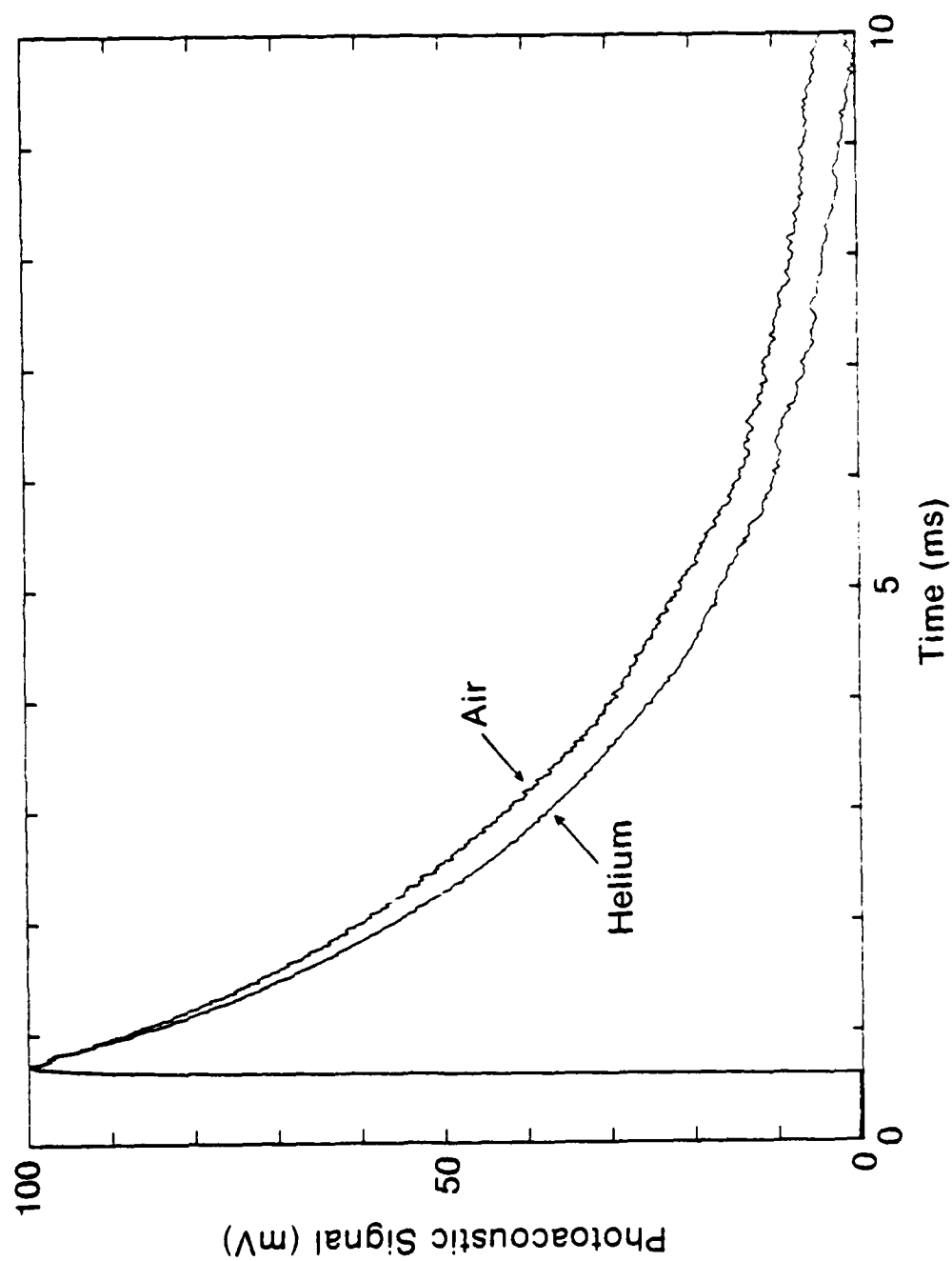
Figure 4. Pulse shape of the calorimeter in air and in a helium atmosphere, excited with a 10 mJ, 12 nsec laser pulse.
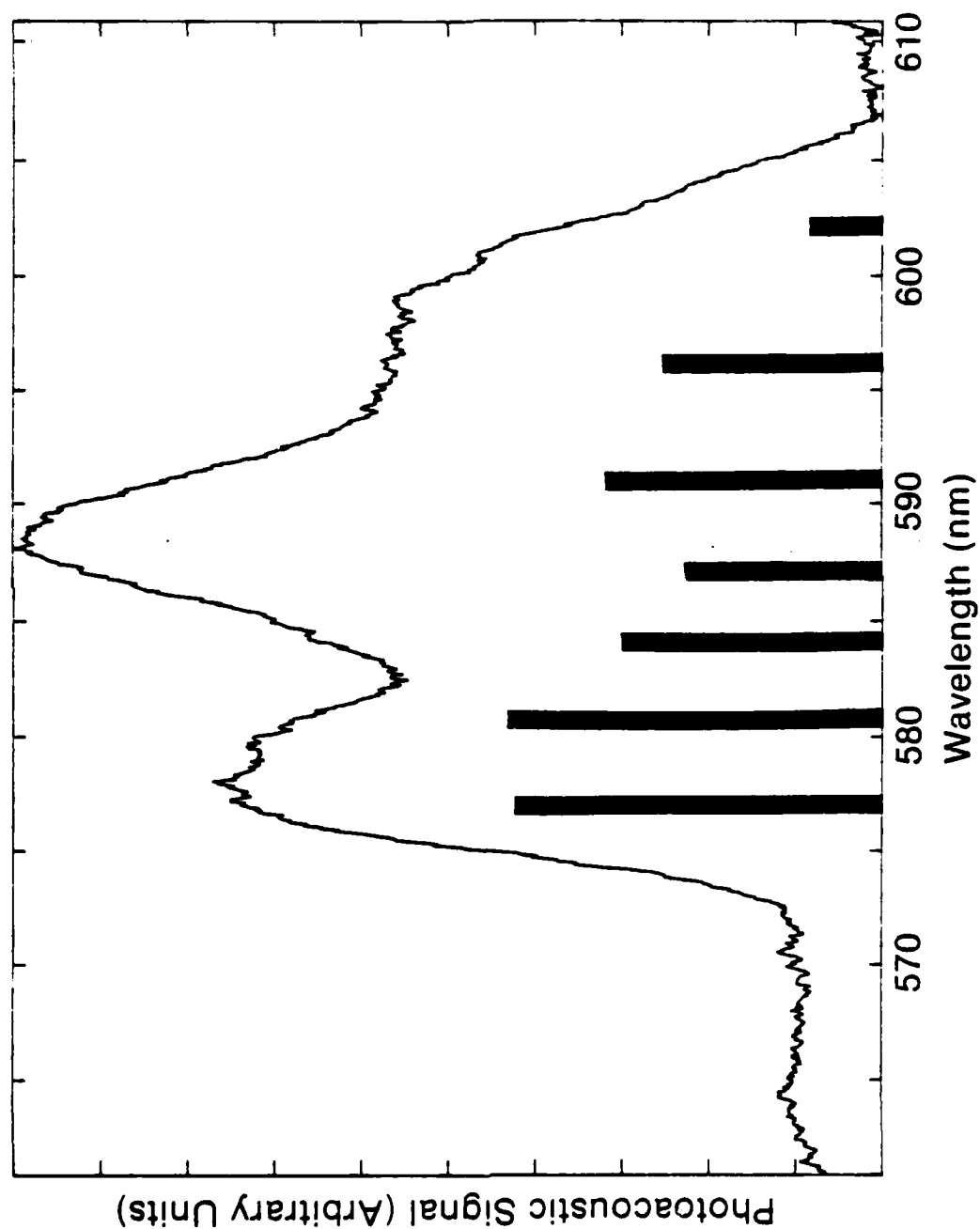
Figure 5. Photothermal absorption spectrum of 0.8×10^{15} Nd_2O_3 molecules isolated on a 10 μm thick PMMA matrix recorded with a pulsed dye laser: resolution 0.006 nm, total number of laser pulses 1000, energy per pulse < 10 mJ. Lines represent absorption data [10] corrected for laser power.

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